

A STUDY ON THE VOLTAMMETRIC BEHAVIOUR OF SILVER ON ELECTRODISPERSED PLATINUM ELECTRODES IN ACID SOLUTION

M. E. MARTINS, R. C. SALVAREZZA and A. J. ARVIA

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Universidad Nacional de La Plata, Sucursal 4, Casilla de Correo 16, (1900) La Plata, Argentina

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Abstract—The early stages of Ag electrodeposition on columnar structured Pt electrodes was investigated in acid solutions covering the underpotential deposition (upd) and overpotential deposition (opd) ranges. Results show a remarkable dependence of the Ag growth mode on the electrode roughness and potential sweep rate. At high potential sweep rates and large substrate roughness factors a 3-D to 2-D rearrangement can be detected. This process appears to be also accompanied by a Pt–Ag formation. For this type of electrode, both processes hinder the nucleation and growth of the 3-D Ag phase. Under certain conditions the complete Ag plating of the entire porous structure can be produced and the voltammetric behaviour of the system then approaches that observed for the Ag/Ag⁺ electrode reaction at an electrochemical thin layer cell.

Key words: metal electrodeposition, electrode roughness, growth modes, microcolumnar structured metal electrodes, porous structures.

INTRODUCTION

Platinum electrodes with a reproducible surface texture and a variable degree of surface roughness can be obtained *in situ* by electroreducing hydrous Pt oxide layers accumulated under a periodic perturbing potential routine in acid or alkaline solutions[1–3]. This type of platinum electrode (hereafter denoted as electrodispersed Pt electrodes, EDPtE), show electroreflectance[4], ellipsometric[5] and impedance[6] characteristics which are typical of rough metal surfaces. The structure of EDPtE as concluded from STM[7], STM-SEM[8] and ellipsometry[5] data, can be described as a columnar microstructure[7] similar to that found in metal deposition from vapour[9]. Furthermore, the EDPtEs exhibit specific electrocatalytic properties for several reactions[10, 11].

The Ag/Ag⁺ electrode reactions have been extensively investigated both in the underpotential (upd) and the overpotential (opd) ranges by using polycrystalline mirror polished Pt[12–14], Pt single crystals[15], and electrochemically faceted Pt electrodes[16]. The present paper describes the behaviour of the Ag/Ag⁺ electrode reactions on EDPtEs of different roughness with the following main purposes: (i) to establish the voltammetric conditions for Ag upd and Ag opd on this type of electrode; (ii) to determine the influence of the applied potential routine on the electrochemical reaction, particularly concerning the non-uniform accessibility of the rough metal surface; (iii) to establish whether under certain conditions the voids of the columnar structure could approach the voltammetric behaviour of a thin layer cell electrode for the Ag/Ag⁺ electrode reactions. The latter opens the possibility of new electrode designs for trace electroanalysis by combining the advantages

of a large electrode surface area and those of thin layer voltammetry.

EXPERIMENTAL

The starting working electrode material was a polycrystalline (pc) platinum wire (99.99% purity, 0.05 cm² geometric area) encased in a glass holder. The electrochemical cell was completed with a platinum counter electrode (4 cm² apparent area). A reversible hydrogen electrode (*rhe*) in the same electrolyte solution was used as reference. Two electrolyte solutions were used, namely 1 M H₂SO₄ + 5 × 10^{−4} M Ag₂SO₄ and 1 M H₂SO₄, the latter being employed for blank experiments. On the basis of previously reported data, the chosen Ag₂SO₄ concentration was considered as the most appropriate for the present purpose[13]. Solutions were prepared from p.a. quality chemicals and Milli-Q* water. Runs were made at 25°C under nitrogen saturation.

The EDPtEs were made in 1 M H₂SO₄ by using a technique described elsewhere[1–3]. It consisted of two stages, the first implying the accumulation of a hydrous platinum oxide layer (HPtOL) on the starting pc Pt electrode, and the second the electroreduction of the HPtOL to produce the EDPtE. The first stage proceeds through the application of a square wave potential routine at 4 kHz between 0.05 and 1.4 V (*vs rhe*) for a time (*ta*) between 30 s and 3 min depending on the preset roughness factor (*R*) value. The second stage was the potentiodynamic electroreduction of HPtOL at 0.001 V s^{−1}. In this way values of *R* ranging between 10 and 100 could be obtained.

The value of R was defined as the $(Q_H)/(Q_{HI})$ ratio, where (Q_H) and (Q_{HI}) are the H-atom electrodesorption voltammetric charge for the EDPtE and that for the starting Pt electrode, respectively, both charges being measured in 1 M H_2SO_4 under the same voltammetric conditions. Similar values of R were obtained by using the corresponding O-atom electrodesorption charge, at least when voltammetry was run at $0.1 V s^{-1}$ between 0.05 and 1.45 V. As recently prepared EDPtEs exhibit a slow roughness decay[8], they were first stored in 1 M H_2SO_4 under open circuit, and later employed in the experiments when the change in the value of R was smaller than 1% in 24 h. Nevertheless, the value of R was systematically checked before and after each run.

The Ag/Ag^+ electrode reactions on the EDPtE were studied under different potential routines by changing systematically the operating conditions, as is usually done in potential controlled electrochemical measurements.

RESULTS

1. Reference voltammetry data on bright pc Pt electrodes

The voltammograms run with pc platinum in 1 M $H_2SO_4 + 5 \times 10^{-4} M Ag_2SO_4$ at $0.02 V s^{-1}$ from 0.05 to 1.45 V by either increasing or decreasing stepwise the cathodic switching potentials (Fig 1a and b) show in the negative potential going scan the appearance of peaks Ic and IIc as well as a cathodic limiting current extending from ca 0.4 V downwards. The latter can also be observed in the reverse potential scan, and in this case it is followed by two largely overlapping anodic current peaks (IIIa and IIa), and at high positive potentials by the anodic peak Ia. The display of the different contributions can be better observed as the cathodic switching potential is set increasingly

negative, as the relative contributions of peaks IIIa and IIa become sensitive to the preset cathodic switching potential.

The voltammetric results are consistent with the appearance of at least two conjugated redox systems, namely the pair of peaks Ic/Ia which corresponds to the overlapping O-electrosorption and Ag upd/stripping processes, and the pair of peaks IIc/IIa related to bulk Ag electrodeposition/electrodissolution. On the other hand, peak IIIa can be assigned to the anodic stripping of the second silver layer. In these experiments one can also note that the H-atom electrodesorption processes which are well known at bright pc Pt electrodes, are inhibited. Moreover, in the Ag^+ -ion containing solution, the initiation of the O-electrodesorption is positively shifted (Fig. 2a). It should also be noted that the potential regions of Ag upd and Ag opd which are determined by E_r , the reversible potential of the $Ag/(1 \times 10^{-3} M Ag^+)$, $E_r = 0.62 V$, cannot be clearly established. Furthermore, there is a competition between the Ag upd stripping and the O-atom electrodesorption which can be easily concluded by comparing the voltammograms shown in Figs 1 and 2 with that of the blank.

When the cathodic and anodic switching potentials are set at 0.59 and 1.12 V, respectively, the early stages for both Ag upd and O-atom electroadsorption can be more clearly displayed (Fig. 2b); but when those switching potentials are set at 0.49 and 0.99 V, respectively, only the conjugated pair of peaks IIa/IIc can be observed. These peaks are accompanied by a minor contribution of those related to the O-electrodesorption processes.

2. Voltammetry data obtained on the EDPtE

In general, the voltammograms run with EDPtEs in 1 M $H_2SO_4 + 5 \times 10^{-4} M Ag_2SO_4$ (Fig. 3) are considerably different from those shown in Figs 1 and

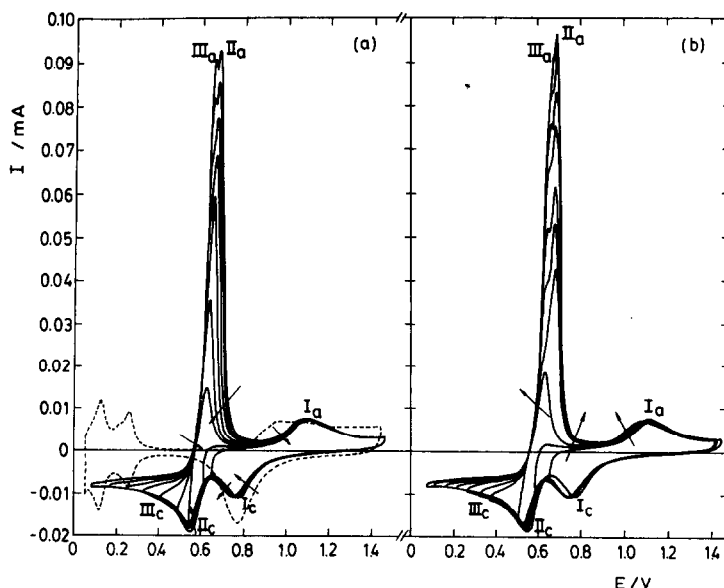


Fig. 1. Cyclic voltammograms obtained on bright Pt (pc) in 1 M H_2SO_4 (---), and in 1 M $H_2SO_4 + 5 \times 10^{-4} M Ag_2SO_4$ (—). Cathodic switching potential either decreased (a) or increased (b) stepwise, $v = 0.02 V s^{-1}$; $25^\circ C$.

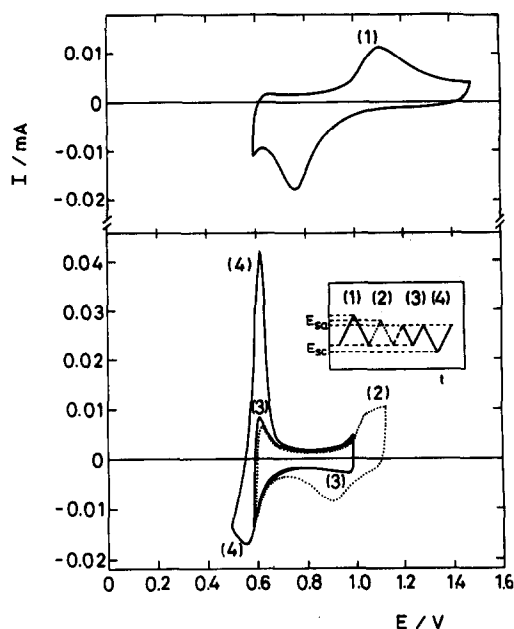


Fig. 2. Cyclovoltammograms obtained on bright Pt (pc) in 1 M $\text{H}_2\text{SO}_4 + 5 \times 10^{-4}$ M Ag_2SO_4 at $v = 0.02 \text{ V s}^{-1}$, 25°C , by changing the potential limits in the subsequent potential cycles as indicated by the numbers and traces in both the potential routine (inset) and the voltammograms. (1) $E_{s,c} = 0.59 \text{ V}$ and $E_{s,a} = 1.47 \text{ V}$; (2) $E_{s,c} = 0.59 \text{ V}$ and $E_{s,a} = 1.12 \text{ V}$; (3) $E_{s,a} = 0.99 \text{ V}$ and $E_{s,c} = 0.59 \text{ V}$; (4) $E_{s,a} = 0.99 \text{ V}$ and $E_{s,c} = 0.49 \text{ V}$.

2 for pc Pt electrodes under the same operating conditions. Furthermore, this difference strongly depends on the value of R (Fig. 3a–c). The corresponding voltammograms for all the values of R show that peak IIc appears only as a shoulder for relatively large values of R ($R = 10$ and $R = 40$), in contrast to the well-defined conjugated pair of peaks IIa/IIc. Furthermore, for $R = 70$, the pair of peaks IIc/IIa is no longer observed (Fig. 3c). Otherwise, the contribution of peaks Ia and Ic becomes better defined as R increases. Furthermore, the EDPtEs show a partial and selective inhibition of the H-atom electro-sorption reactions, together with a shift of the entire voltammogram downwards due to the Ag electrodeposition reaction. Both effects, however, tend to disappear very rapidly as R increases, the voltammograms approaching that of the blank.

The electroreduction voltammograms indicate that once bare Pt sites become available at the electrode surface, Ag upd electrodeposition begins to take place. Then, the voltammetric response of the system suggests that a portion of the Pt surface becomes covered by a more or less uniform Ag layer. The remaining bare Pt surface in contact with the Ag^+ -ion-free acid solution becomes responsible for the appearance of the H-atom electro-sorption peaks.

The precedent results suggest the convenience of running an experiment with an EDPtE consisting of a potential cycling as earlier indicated in 1 M $\text{H}_2\text{SO}_4 + 5 \times 10^{-4}$ M Ag_2SO_4 and leaving the electrode 24 h, immersed in the electrolyte solution under open circuit conditions. Afterwards, the voltammetric behaviour of the EDPtE corresponds to that of the

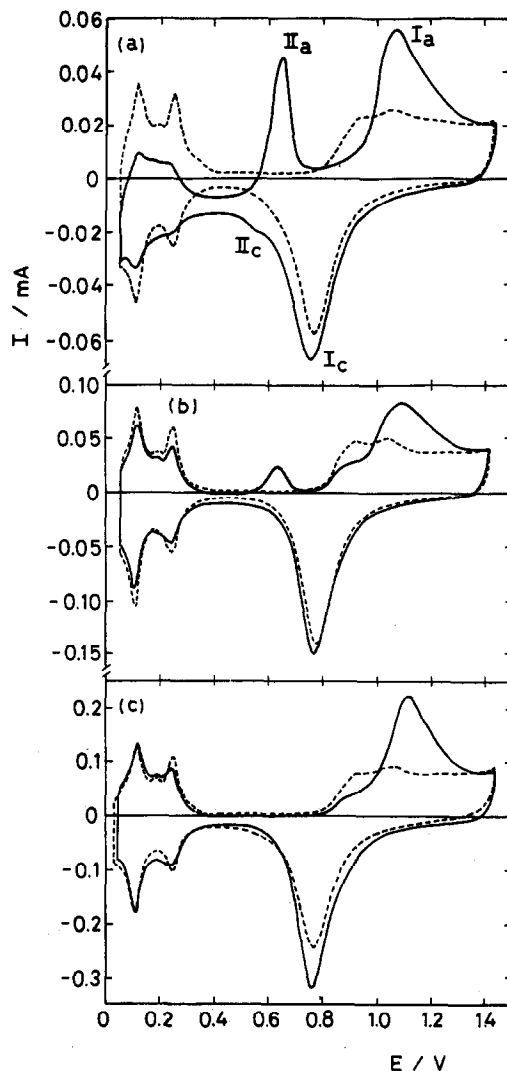


Fig. 3. Cyclovoltammograms obtained with EDPtE in 1 M $\text{H}_2\text{SO}_4 + 5 \times 10^{-4}$ M Ag_2SO_4 (—) and in 1 M H_2SO_4 (---) at 0.02 V s^{-1} , 25°C . (a) $R = 10$; (b) $R = 40$; (c) $R = 70$.

reversible Ag/Ag^+ electrode reactions occurring at a large area Ag electrode. In this case the Ag plating depends on the immersion time in the Ag^+ -ion-containing solution which is required for the porous structure to be completely filled with Ag^+ -ions from the solution. This immersion time increases according to the value of R . Correspondingly, the open circuit potential becomes very close to the E_r value. Under these circumstances, the cyclovoltammogram resulting for the Ag plated EDPtE presents the typical voltammogram of the Ag/Ag^+ -ion electrode processes in a thin layer electrochemical cell (Fig. 4a). However, one can observe that the heights of the anodic and cathodic current peaks in the cyclovoltammograms decrease gradually along cycling approaching the features already described for the EDPtE substrate (Fig. 4b). In this case, the number of cycles required to approach the initial voltammogram increases with both the value of R and the EDPtE immersion time into the Ag^+ -ion-containing solution under open circuit conditions. A similar

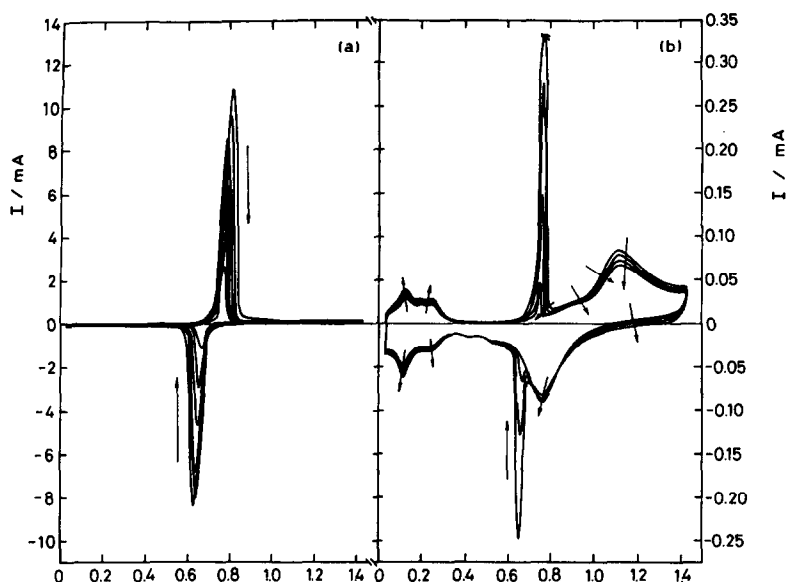


Fig. 4. Cyclovoltammograms obtained with EDPtE ($R = 40$) in 1 M H_2SO_4 at 0.02 V s^{-1} , 25°C . The electrode has been previously potential cycled and then left during 24 h in the Ag^+ -ion containing solution at open circuit.

voltammetric response can also be obtained when the Ag plated EDPtE is cycled in plain 1 M H_2SO_4 . The latter experiment also provides quantitative information about the amount of Ag deposited under open circuit conditions.

3. The influence of potential scan rate on the voltammetric response of the Ag/Ag^+ electrode processes on EDPtE

Further details of the Ag/Ag^+ -ion electrode processes in 1 M H_2SO_4 on EDPtE, particularly in relation to the EDPtE structure, can be derived from the voltammograms (Fig. 5) recorded in the Ag^+ -ion-containing solution at $0.001 \text{ V s}^{-1} < \nu < 0.2 \text{ V s}^{-1}$ by changing R from 10 to 70. These results show that for very low values of ν (Fig. 5a) the H-electrosorption processes are already largely inhibited, whereas the Ag/Ag^+ -ion electrode processes are considerably enhanced (peaks IIa/IIc). In this case the Ag electrodeposition limiting current can be clearly observed, and the first O-electrodesorption stage (peak I'a) is appreciably diminished. Otherwise, those voltammograms obtained in the $0.01 \text{ V s}^{-1} < \nu < 0.2 \text{ V s}^{-1}$ range (Fig. 5b and c), exhibit a clearer definition of those peaks related to the H-electrosorption processes as ν increases. The same trend is observed for the O-electrosorption peaks, although in this case the contribution of the Ag/Ag^+ -ion electrode processes are strongly diminished.

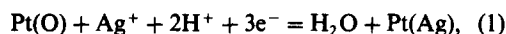
DISCUSSION

The present results demonstrate the influence of the roughness substrate characteristics on the complex processes taking place on both the upd and opd metal layer formation, particularly when the experiments are made at relatively high potential sweep rates. In the present case, new processes coupled to the proper

Ag/Ag^+ electrode reactions can be distinguished by using adequate values of R and voltammetry conditions.

1. Early stages of Ag electrodeposition and O-monolayer electroreduction

The conjugated overall reactions related to peaks Ic/Ia can be expressed by the following equation in both directions, respectively[12–16]:



where the parentheses denote surface species at the Pt substrate. Reaction (1) in the forward direction corresponds to the formation of the first monolayer of Ag upd competing with the O-adatom electrodesorption.

On the other hand, peak IIc corresponds to a complex peak involving the nucleation and growth of a second Ag layer at E_r , and bulk Ag electrodeposition, both processes undergoing under-diffusion control[13, 16, 17]. These two processes are mainly concerned with Ag–Ag interactions, in contrast to those described by reaction (1) which comprises principally Ag–Pt and Pt–O interactions. During the positive potential going scan, bulk Ag and the second Ag layer are simultaneously electro-dissolved in the potential range of peaks IIIa–IIa.

2. Silver layer growth modes

A close inspection of the results shown in Fig. 3, run at a relatively high potential sweep rate, indicates that the total Ag electrodeposited charge on the different EDPtEs increases with R although the corresponding charge density referred to the real active surface area of the substrate decreases as R increases. Correspondingly, one can observe that the contribution of both bulk Ag and second Ag layer growth decreases as R increases, in contrast to the contribution of the Ag monolayer which remains practically independent of the R value. This means that in

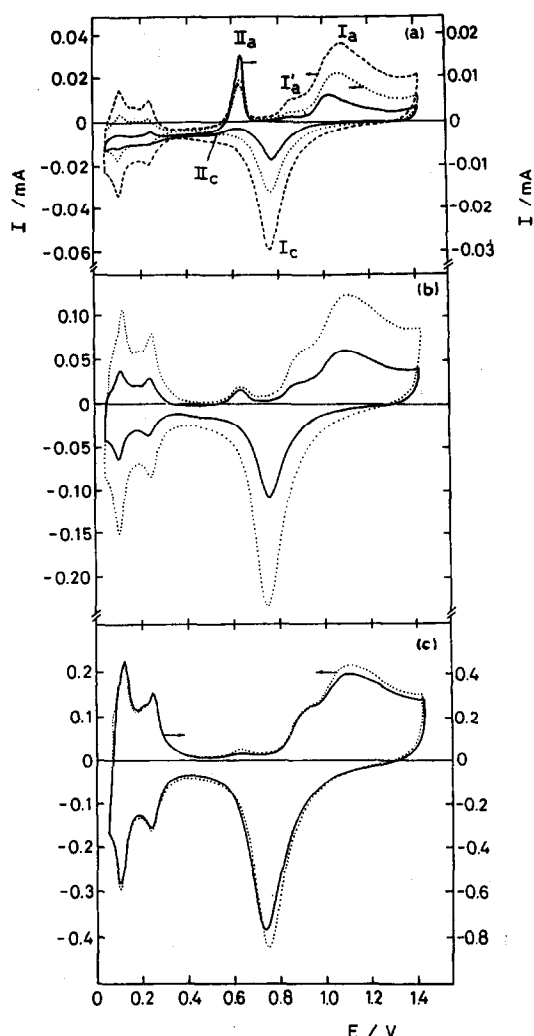


Fig. 5. Cyclovoltammograms obtained with EDPTe ($R = 40$) in $1 \text{ M H}_2\text{SO}_4 + 5 \times 10^{-4} \text{ M Ag}_2\text{SO}_4$ at different potential sweep rates; 25°C . (a) (—) 0.001 V s^{-1} ; (···) 0.005 V s^{-1} ; (—) 0.01 V s^{-1} . (b) (—) 0.02 V s^{-1} ; (···) 0.05 V s^{-1} . (c) (—) 0.1 V s^{-1} ; (···) 0.2 V s^{-1} .

this case the relative number of Ag–Ag and Ag–Pt bonds contributing to the Ag layer growth depend on R . Then, the ratio between the total amount of electrodeposited Ag (second Ag plus bulk Ag) and that of the Ag monolayer on the Pt substrate decreases as R changes from 10 to 70. This fact cannot be exclusively explained in terms of the columnar microstructure of the EDPTe as in this case one would expect that Ag electrodeposition would occur preferentially at tip sites of the columns, the voids between columns remaining as Ag-free sites which are active for either H- or O-electrosorption. These considerations would imply that the effective substrate area for Ag electrodeposition at high potential sweep rates, would not differ markedly as R increases.

For the diffusion controlled Ag^+ ion electrodeposition under high potential sweep rate, the overlapping of the radial diffusion fields at the tips would result in a linear monodirectional diffusion field so that only the outer surface of the rough substrate would act as a collecting plane for the arriving Ag^+

ions, so there would be no reason for expecting a complete inhibition of second layer and bulk Ag electrodeposition. However, Ag electrodeposition on the tip domains of the columnar microstructure generates at least two concentration gradients for Ag atoms, one between the tip domain and the wall and the bottom of the intercolumnar voids, and another between the growing Ag centres and the bulk substrate. In this respect, it should be noted that Ag atoms exhibit a greater surface mobility than Pt atoms at room temperature[18]. Considering that the Ag–Pt bond is stronger than the Ag–Ag bond, the arriving Ag^+ ions contacting Pt sites should be more probably attached to those sites, whereas those ones sticking to Ag-covered domains can diffuse a relatively large distance to reach a free Pt site for final attachment. This fact results in a net flux of Ag atoms from tips to valleys of the porous structure to produce a Ag layer more uniformly distributed on the Pt substrate. Consequently, the early stage of bulk Ag electrodeposition should be to some extent hindered, and the growth of Ag centres on EDPTes should be envisaged as a transient process whose half-life time is shorter than the half-life time of mass transport processes at the surface. The above-described processes can be described as a 3-D to 2-D rearrangement provided that free Pt sites become available.

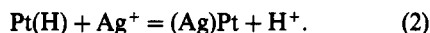
Another interesting facet of these results (Fig. 3) is that the contribution of the H-electrosorption processes increase as R increases reaching for $R = 70$ a value very close to that of the blank without observing the corresponding reduction of the Ag electrodeposit at the monolayer level. Thus, one should consider two additional processes, namely the possible penetration of Ag atoms underneath coupled to the displacement of Pt atoms on the substrate surface to allow bulk diffusion of Ag atoms. This implies that Ag atoms have two options, either to diffuse on the Ag surface layer or to diffuse into bulk Pt to form a sort of alloy skin. As a matter of fact, it was reported that the stripping of Ag from a Pt electrode when a Ag–Pt alloy has formed, takes place at 1.2 V , just in the potential range of peak Ia where the Ag monolayer is also anodically stripped[13, 14].

The Ag–Pt alloying competes with the Ag layer growth. Accordingly, bulk Ag formation would be hindered if either Pt free sites are available or Ag-atoms have enough time to diffuse into Pt. Both processes produce a dilution of Ag-atoms either by the excess of surface present in the columnar microstructure (free Pt sites) or by moving Ag-atoms into bulk Pt. For EDPTe the nucleation and growth of bulk Ag requires more time (charge) than on a conventional smooth substrate.

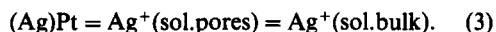
3. The Ag^+ –H atom displacement reaction and the Ag/Ag^+ electrode reaction at pores

The voltammetric features obtained on the EDPTes can be reasonably explained on the basis of the precedent analysis. At low v , all the columnar structure becomes Ag plated as there is enough time for Ag^+ -ions to diffuse from the bulk of the solution to the voids of the columnar structure. Conversely, at high v , there is only a relatively small amount of

Ag deposited compared with the large number of free Pt sites available. Hence, the accessibility of the electrode surface to the reacting species is greatly limited. This fact can be unambiguously demonstrated through the spontaneous Ag plating of the previously H-atom-covered EDPtE surface at open circuit. This process can be associated with the displacement of H atoms by Ag^+ ions at the porous Pt structure, according to a reaction such as:



Reaction (2) under the present conditions is thermodynamically feasible. Accordingly, when the porous structure is filled with Ag^+ ion-containing solution, the reaction at pores during potential cycling (Fig. 4) is:



The voltammetric characteristics of reaction (3) at pores approaches very closely those reported for the same reaction in thin cell voltammetry[19].

CONCLUSIONS

The precedent results point out that there are two limiting cases for the voltammetric behaviour of Ag/Ag^+ -ion electrode reactions on EDPtE. The first corresponds to that of a very low potential scan rate in which the voltammograms approach that obtained for bright pc Pt. In this case, Ag^+ -ions have a sufficiently long diffusion length to be deposited on the entire rough Pt surface, leaving only a few surface sites free for either H- or O-atom electrosorption. Another limiting case appears at high scan rates where the behaviour is totally opposed to that previously described. In fact, Ag^+ -ions are then deposited only on those sites which become easily accessible (tip domains), while H- and O-atoms occupy Ag-free Pt sites (wall and bottom domains). Hence, the voltammograms approach that of the blank. Under these conditions the 3-D to 2-D Ag layer rearrangement can be concluded.

A similar behaviour can be observed for EDPtEs at a constant v and variable R . At low values of R the voltammetric features become similar to those found at low v values, whereas for high R values results are comparable with those obtained at high v values.

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